Noble metal catalyzed aqueous phase hydrogenation and hydrodeoxygenation of lignin-derived pyrolysis oil and related model compounds

CrossMark

Wei Mu [a], Haoxi Ben [b], Xiaotang Du [a], Xiaodan Zhang [c], Fan Hu [b], Wei Liu [a], Arthur J. Ragauskas [d], Yulin Deng [a,*]

[a] School of Chemical and Biomolecular Engineering, Renewable Bioproducts Institute, Georgia Institute of Technology, Atlanta, GA 30318, United States
[b] Department of Chemistry and Biochemistry, Institute of Paper Science and Technology, Georgia Institute of Technology, Atlanta, GA 30318, United States
[c] School of Material Science and Engineering, Institute of Paper Science and Technology, Georgia Institute of Technology, Atlanta, GA 30318, United States
[d] Department of Chemical and Biomolecular Engineering, Center for Renewable Carbon, University of Tennessee, Knoxville, TN 37996, United States

HIGHLIGHTS

- Three model compounds were used to study the lignin derived heavy oil upgrading.
- Four noble metal catalysts were evaluated and the reaction mechanism was deduced.
- The coking induced catalyst deactivation was systematically studied and characterized.
- Two catalysts (Pt and Ru) were picked for lignin heavy oil upgrading.
- Tentative reaction path of oil upgrading matches mechanism from model compound study.

GRAPHICAL ABSTRACT
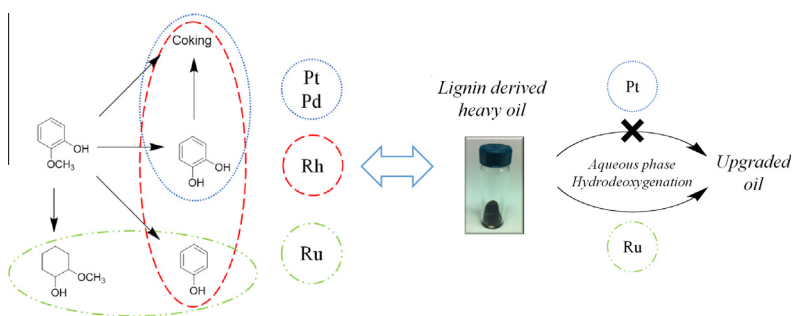
ABSTRACT

Aqueous phase hydrodeoxygenation of lignin pyrolysis oil and related model compounds were investigated using four noble metals supported on activated carbon. The hydrodeoxygenation of guaiacol has three major reaction pathways and the demethylation reaction, mainly catalyzed by Pd, Pt and Rh, produces catechol as the products. The presence of catechol and guaiacol in the reaction is responsible for the coke formation and the catalysts deactivation. As expected, there was a significant decrease in the specific surface area of Pd, Pt and Rh catalysts during the catalytic reaction because of the coke deposition. In contrast, no catechol was produced from guaiacol when Ru was used so a completely hydrogenation was accomplished. The lignin pyrolysis oil upgrading with Pt and Ru catalysts further validated the reaction mechanism deduced from model compounds. Fully hydrogenated bio-oil was produced with Ru catalyst.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The growth of global energy consumption makes biofuel an attractive alternative fuel source. Lignin, the second most abundant nature-made polymer, receives little attention because of its

* Corresponding author. Tel.: +1 404 894 5759.
  E-mail address: yulin.deng@chbe.gatech.edu (Y. Deng).

complex structure and poor thermal stability. The US paper industry produces over 50 million tons of lignin per year. Over 98% of it is burned directly (Calvo-Flores and Dobado, 2010). Another major source of lignin is bioethanol plant. Regardless of the technology employed, almost all bioprocessing approaches result in the formation of a waste lignin process stream (Wyman, 2007). Different from other biomass wastes, lignin is energy-rich. Therefore it is pragmatic and desirable to find an efficient approach to convert lignin into fuel and useful chemicals.

Pyrolysis is an economical and feasible approach for lignin conversion (Maschio et al., 1992). Slow pyrolysis produces heavy oil and light oil (Mohan et al., 2006). Heavy oil consists of compounds that are water-insoluble. The molecular structures in heavy oil are mainly dimers and trimers. Light oil is mostly composed of water-soluble monomers. Both oil products possess several poor properties, such as thermal instability, corrosiveness, low volatility, high coking tendency, low heating value, and immiscible with petroleum fuels (Mu et al., 2013). Further upgrading of pyrolysis oil provides insight into the conversion from biomass to fuels.

Hydrodeoxygenation (HDO) has been widely used for pyrolysis bio-oil upgrading (Furimsky, 2000). Noble metal catalysts are very reactive in HDO reactions. The performance of the commonly used noble metal catalysts for HDO reaction was reviewed in our previous publication (Mu et al., 2013). The sulfur-induced noble metal catalyst deactivation does not pose a problem in this study because biomass contains a small amount of sulfur. Most of the studies reported in the review paper were done under various conditions with different supporting materials, making the evaluation of catalytic performance very difficult.

The purpose of this study is to compare the performance of commonly used noble metal catalysts at similar condition to understand the mechanism differences between noble metal catalysts in HDO reaction. Four noble metal catalysts (Pd, Pt, Rh, Ru) were used with activated carbon being the support material. Compared to oxidic supports, activated carbon is suitable to study the catalytic behavior of active metal without interference due to its neutral surface and little interaction with metals (Furimsky, 2008). DI water with pH 7 was used as dispersant in the reaction. The neutral aqueous phase can reveal the genuine catalytic behavior of the noble metals. By understanding the detailed reaction mechanism from model compound study, two catalysts with low and high robustness were picked and applied to real lignin derived pyrolysis oil.

2. Methods

2.1. Lignin purification and process of pyrolysis

The milled pinewood was ethanol-organosolv pretreated as previously described in literature (Hallac et al., 2010). Pyrolysis experiments were conducted in a quartz tube heated with a split-tube furnace. The experiment condition can be found in previous publication (Ben and Ragauskas, 2011a).

2.2. Hydrogenation reaction for model compounds and EOL heavy oil

All catalysts used in this study were purchased from Sigma–Aldrich. The catalysts were used directly without any pretreatment. HDO of both model compounds and EOL heavy oil were carried out in a 75 mL Parr 4590 Micro Stirred Reactor. One step HDO was used in model compounds study. In a typical run, 25 mmol model compound and 20 mL DI water were loaded in a glass liner with 50.0 mg of 5 wt% noble metal catalyst. The reactor was purged 5 times with nitrogen gas and then 5 times with hydrogen gas consecutively. When the target temperature was

reached, the reactor is pressurized with hydrogen gas to 4.0 MPa. The reaction was conducted under 250 °C for 2 h.

For EOL heavy oil, HDO reaction was performed in two steps. In the first step, 150.0 mg of heavy oil and 20.00 mL of DI water were loaded in a glass liner with 15.0 mg of noble metal catalyst. The reactor was purged 5 times with nitrogen gas and then 5 times with hydrogen gas consecutively. The reactor was heated at 300 °C for 4 h and the pressure was stable at ∼14 MPa. The aqueous solution of the products was filtered through a 0.45 μm PTFE syringe filter to remove the spent catalyst. The filtrate was further upgraded by the second step of HDO, which was conducted at 250 °C for 2 h with the initial hydrogen pressure of 10 MPa and 10.0 mg fresh catalyst.

2.3. Characterization of catalysts and oil products

BET surface area measurements of the catalysts were carried out in a Quadrasorb system from Quantachrome instruments. Metal dispersions were measured in a AutoChem II 2920. TEM images were taken with a JEOL 100CX II 100 kV. The carbon contents of the upgraded bio-oil were determined by total organic carbon (TOC) analyzer (Ionics Inc 1555B). All products were characterized by a Bruker Avance/DMX 400 MHz NMR spectrometer. The detailed parameters were reported in previous publications. (Ben and Ragauskas, 2011a,b)

3. Results and discussion

3.1. Reactivity with model compounds

Phenol, catechol and guaiacol are commonly used as model compounds to study the reaction mechanism of lignin pyrolysis oil upgrading. The conversions of these model compounds for all four catalysts are summarized in Fig. 1(a). As shown in Fig. S1 (see Supplementary Information), three major reaction pathways are observed in the HDO of guaiacol: (1) direct hydrogenation of aromatic ring, (2) demethylation reaction and (3) demethoxylation reaction. No transalkylation reaction is observed due to the use of a carbon support. For phenol and catechol, all four catalysts show similar reactivity. However, both Pt and Pd catalysts could not catalyze the HDO reaction of guaiacol.

The experimental result with different guaiacol/catalyst weight ratios is shown in Fig. 1(b). Ru was the best catalyst at all ratios. When the weight ratio was 20, the conversion of Ru catalyzed guaiacol HDO was almost 100%. Rh was the second best catalyst. When the weight ratio of guaiacol to the catalyst was decreased, the difference in the conversion of guaiacol with Ru and Rh catalysts was also decreased. Pt and Pd catalysts had approximately zero guaiacol conversion at a weight ratio of 20 and 60. When the weight ratio was decreased to 2, the conversions were over 80%.

3.1.1. Platinum and palladium catalyzed guaiacol HDO

Runnebaum et al. reported that demethylation was a fast reaction step in the HDO of guaiacol using Pt catalyst, which yielded catechol (Runnebaum et al., 2012). Another paper demonstrated that coke was formed with the presence of both guaiacol and catechol (Furimsky, 2000). It is reasonable to propose that the presence of guaiacol and catechol deactivates both Pt and Pd catalysts. To validate this hypothesis, three groups of control experiments were performed and summarized in Table S1 (see Supplementary Information).

In group 1, Ru catalyst was used in the HDO reaction of both guaiacol and catechol because Ru exhibits excellent reactivity with guaiacol or catechol individually. The low guaiacol conversion
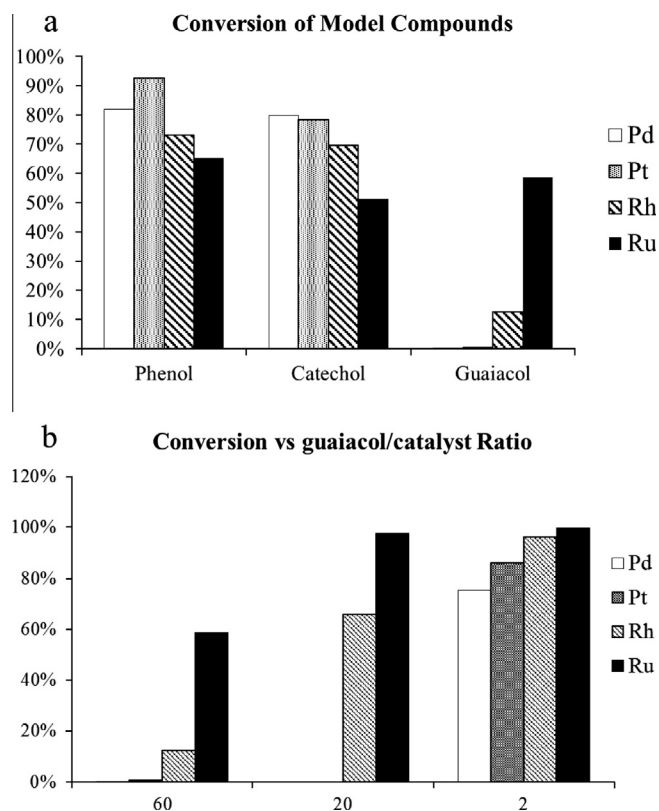
Fig. 1. (a) Conversion of model compounds with different catalysts. Reaction condition: 50 mg catalyst, 25 mmol model compounds, 250 °C, 40 bar H$_2$, 2 h. (b) Conversions with different guaiacol/catalyst ratio. Reaction condition: 25 mmol (3.1 g) guaiacol, 250 °C, 40 bar H$_2$, 2 h.

indicates Ru is deactivated in the presence of guaiacol and catechol. In group 2, Pt and Pd were used to catalyze the HDO reaction of guaiacol and phenol aqueous mixture, respectively. Pt and Pd catalyzed phenol hydrogenation effectively. In the presence of guaiacol, almost no phenol was hydrogenated, which meant that the catalysts were deactivated in the presence of guaiacol. In the last group, carbon monoxide was added in the gas phase. It was reported that CO was produced when Pt was used in the HDO of guaiacol and CO was another potential cause of catalyst deactivation. The result turns out that both Pt and Pd are still able to catalyze phenol hydrogenation with the existence of a relatively high amount CO in the gas phase. Therefore, catalyst deactivation is mainly caused by coke generated from guaiacol and catechol.

3.1.2. Rhodium catalyzed guaiacol HDO

The product distribution of Rh catalyzed guaiacol HDO is shown in Fig. 2(a). The overall conversion was around 12% after 4 h reaction. Phenol, cyclohexanone, cyclohexanol and 1,2-cyclohexanediol were the main products. The distribution of products did not show remarkable change after 1 h, indicating the deactivation of Rh catalyst.

Experimental results show that the demethoxylation of guaiacol, which produced phenol at high selectivity, is a fast reaction for Rh catalyst. 2-Methoxy-cyclohexanol was not detected in the solution, which suggests that there is no direct hydrogenation reaction. The existence of 1,2-cyclohexane-diol, with selectivity around 15%, indicates that catechol is the intermediate product from the HDO of guaiacol. The experimental data shows that Rh was also deactivated by coke formation from guaiacol and catechol. Unlike Pt and Pd, which catalyzes demethylation reaction very efficiently, both catalysts were almost deactivated immedi-

ately after the reaction began. The demethylation reaction catalyzed by Rh is a relatively slow step. The reactivity decays slowly and it was completely deactivated after 2 h. The proposed reaction path is shown in Fig. S2a (see Supplementary Information).

3.1.3. Ruthenium catalyzed guaiacol HDO

The product distribution in the HDO of guaiacol by Ru is shown in Fig. 2(b). Ruthenium got the highest conversion among all four catalysts. Cyclohexanol and 2-methoxy-cyclohexanol were the main products. Phenol was the key intermediate product in the beginning of the reaction. The yield of phenol was around 20% after 15 min and gradually converted to cyclohexanol after four hours. 1,2-cyclohexanediol is a minor intermediate product. Compared to Rh in the same reaction, which produced 1,2-cyclohexanediol at the beginning of the reaction, 1,2-cyclohexanediol was not observed in the first 60 min for Ru. After 90 min, only 2% of 1,2-cyclohexanediol was detected, indicating that it was not likely to be produced directly from guaiacol. One possible reaction for the generation of 1,2-cyclohexanediol is the hydrolysis of 2-methoxy cyclohexanol. The proposed reaction mechanism of the HDO of guaiacol by Ru is shown in Fig. S2(b) (see Supplementary Information). No catechol was detected throughout the reaction, which prevented the formation of coke.

3.2. Characterization of catalyst

The physisorption and chemisorption results of all four catalysts were characterized before reaction without any pretreatment. The results are Table S2 (see Supplementary Information). The dispersions of active metals indicated the percentage of metallic atoms contribution for reactant adsorption. Rh/C has the highest dispersion, followed by Ru/C, Pt/C and Pd/C. All catalysts have similar surface area and pore radius before the reaction, as the support is activated carbon obtained from the same source.

BET results and TEM pictures of the spent catalysts are shown in Fig. S3 (see Supplementary Information). The experimental results from the studies of model compounds match the BET data in Fig. S3(a) very well. The surface area of Pd and Pt catalysts decreased by 36.96% and 48.60%, respectively. The significant reduction in surface area indicated the existence of severe coke formation. For Rh, the surface area reduced by 27.97%, which is less than the value of Pt and Pd. There was only an 11.97% decrease in surface area for Ru. The pore size of all the catalysts was also calculated. No significant decrease in the pore size was observed due to the neutral surface of carbon, which possess small amount of Lewis acid sites (Furimsky, 2008).

The TEM images of the catalysts are shown in Fig. S3(b). These pictures further validate the conclusion drawn from experimental data and BET results. After the reaction, large amount of coke was observed on Pd and Pt catalyst particles. The slow deactivation rate of Rh catalyst leads to uniformly distributed coke throughout the carbon support. Ru catalyst did not show significant changes after the reaction.

3.3. Noble metal catalyzed EOL heavy oil upgrading

To examine whether the reaction mechanism deduced above is applicable to the catalytic HDO of EOL heavy oil, one inactive catalyst (Pt) and the most reactive catalyst (Ru) were chosen to catalyze EOL heavy oil. Two-step HDO reaction was used because of tar formation in the first step HDO reaction. Several studies reported the formation of tar or coke during the HDO of phenolic model compounds (Furimsky, 2000) and water soluble pyrolysis oils (Vispute et al., 2010). The structure and physical property of tar products were discussed in a previous report (Ben et al., 2013).
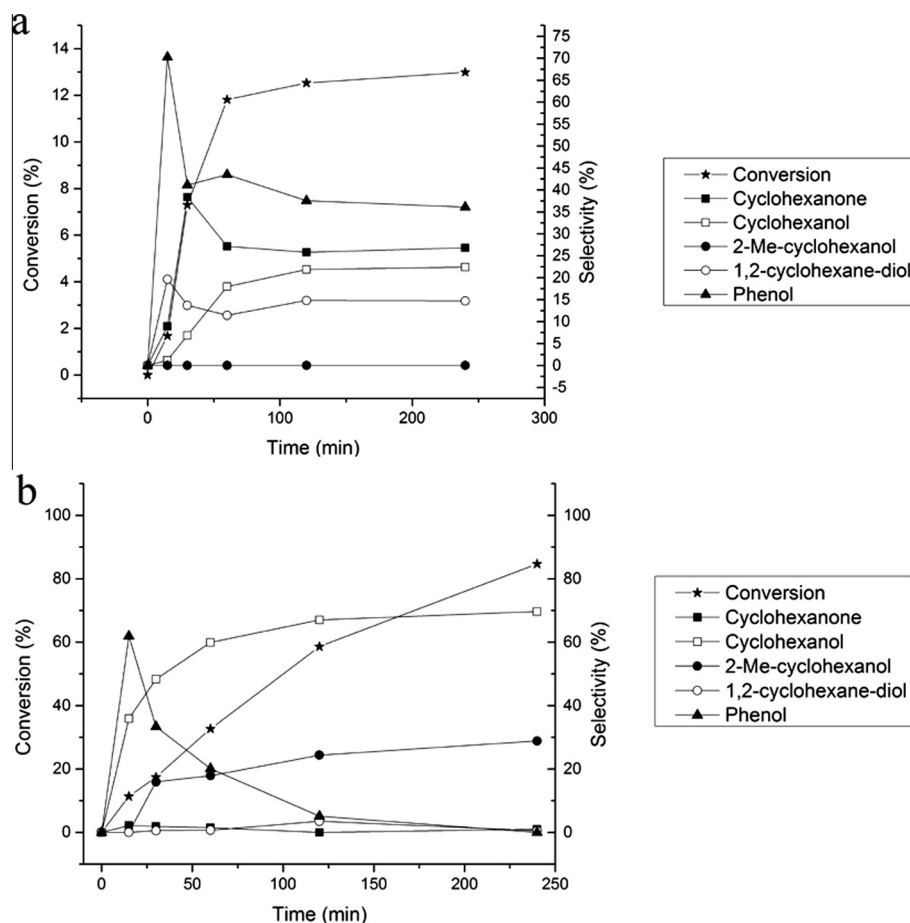
Fig. 2. Product distribution of (a) rhodium catalyzed guaiacol HDO and (b) ruthenium catalyzed guaiacol HDO.

The carbon yields of Ru and Pt are summarized in Table 1. The carbon yield in the first step of HDO was around 30% for both catalysts. There were three significant changes after first HDO reaction. First, compounds which tend to form tar are removed. Second, the heavy oil (M_w = 265) was degraded from dimers and trimers to monomers. Third, water-soluble compounds were obtained from the water-insoluble heavy oil. The carbon yields of the second step reaction were high for both catalysts.

Proton NMR was used to quantify the degree of hydrogenation. The ^{1}H-NMR spectra for the EOL heavy oil and the products after the first and second step upgrading reaction are listed in the Fig. S4 (see Supplementary Information). The integration results are presented in Table 1. The aromatic protons were completely eliminated in the second HDO reaction catalyzed by Ru and 85% of the protons are due to aliphatic protons with no oxygen atoms bonded to the α-carbon. This indicates that the second HDO

reaction products contain only aliphatic carbons and have relatively low oxygen content, which represents a potential resource for bio-gasoline. On the other hand, the products from the second HDO reaction catalyzed by Pt still have 15.73% protons in the aromatic region, which is likely due to guaiacol-based compounds. Each carbon has roughly one hydrogen atom in an aromatic ring and two hydrogen atoms in an aliphatic ring, which means that around 30% of the carbon rings remained aromatic. Pt cannot catalyze the HDO reaction of guaiacol-based compound. Compared with the NMR spectrum of the first HDO reaction products, no significant change was observed after second HDO reaction.

Possible pathways of Ru catalyzed heavy oil upgrading are shown in Fig. S5 (see Supplementary Information). In first HDO reaction, condensation was dominant pathway. This leads to the formation of tar and coke that rapidly deactivates the catalyst. After first HDO reaction, there were large amount of guaiacol

Table 1
^{1}H-NMR and Total organic carbon (TOC) yield of EOL heavy oil and products from first and second step HDO reaction catalyzed by Pt or Ru.

Type of protons	EOL heavy oil	Ru		Pt	
		First Step	Second Step	First step	Second step
—C**H**O, —COO**H**	0[#]	0	0	0	0
Ar**H**, **H**C=C—	31	21	0	24	14
—C**H**$_n$—O—, C**H**$_n$—O—	27	18	15	32	24
—C**H**$_3$, —C**H**$_n$—	42	61	85	44	62
TOC yield		36%	Approx. 100%	28%	95%

The bold "H" stands for the corresponding proton shown in the ^{1}H-NMR.
[#] The results are shown as percentage of hydrogen.

and 4-methyl-guaiacol in the solution. The reaction pathway in the second HDO step is similar to the reaction mechanism for the model compounds. Ru catalyzes either direct hydrogenation or demethoxylation reaction, in which both yield cyclohexanol-based product. GC analysis shows that around 45% of the products in the upgraded oil were cyclohexanol and 4-methyl-cyclohexanol.

4. Conclusion

In summary, four noble metal catalysts were evaluated with three model compounds for neutral aqueous phase hydrodeoxygenation. The major conclusions from this study are (1) Pd, Pt and Rh catalysts were all deactivated during the reaction. The reaction mechanism is discussed; (2) the decrease in surface area and TEM images indicated coke formation on Pt, Pd and Rh catalysts; (3) Ru catalyst fully hydrogenates guaiacol because of the unique reaction pathway. Upgrading of EOL pyrolysis oil with Ru catalyst produces cyclohexanol and 4-methyl-cyclohexanol as main products with 34% carbon yield; (4) the proposed reaction mechanism agrees well with the conclusion drawn from model compound studies.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2014.09.067.

References

Ben, H., Mu, W., Deng, Y., Ragauskas, A.J., 2013. Production of renewable gasoline from aqueous phase hydrogenation of lignin pyrolysis oil. Fuel 103, 1148–1153.

Ben, H., Ragauskas, A.J., 2011a. NMR characterization of pyrolysis oils from kraft lignin. Energy Fuels 25 (5), 2322–2332.

Ben, H., Ragauskas, A.J., 2011b. Pyrolysis of kraft lignin with additives. Energy Fuels 25 (10), 4662–4668.

Calvo-Flores, F.G., Dobado, J.A., 2010. Lignin as renewable raw material. ChemSusChem 3 (11), 1227–1235.

Furimsky, E., 2008. Carbons and Carbon Supported Catalysts in Hydroprocessing. The Royal Society of Chemistry.

Furimsky, E., 2000. Catalytic hydrodeoxygenation. Appl. Catal. A 199 (2), 147–190.

Hallac, B.B., Pu, Y., Ragauskas, A.J., 2010. Chemical transformations of *Buddleja davidii* lignin during ethanol organosolv pretreatment. Energy Fuels 24 (4), 2723–2732.

Maschio, G., Koufopanos, C., Lucchesi, A., 1992. Pyrolysis, a promising route for biomass utilization. Bioresour. Technol. 42 (3), 219–231.

Mohan, D., Pittman, C.U., Steele, P.H., 2006. Pyrolysis of wood/biomass for bio-oil: a critical review. Energy Fuels 20 (3), 848–889.

Mu, W., Ben, H., Ragauskas, A., Deng, Y., 2013. Lignin pyrolysis components and upgrading – technology review. Bioenergy Res. 6 (4), 1183–1204.

Runnebaum, R.C., Nimmanwudipong, T., Block, D.E., Gates, B.C., 2012. Catalytic conversion of compounds representative of lignin-derived bio-oils: a reaction network for guaiacol, anisole, 4-methylanisole, and cyclohexanone conversion catalysed by Pt/[gamma]-Al2O3. Catal. Sci. Technol. 2 (1), 113–118.

Vispute, T.P., Zhang, H., Sanna, A., Xiao, R., Huber, G.W., 2010. Renewable chemical commodity feedstocks from integrated catalytic processing of pyrolysis oils. Science 330 (6008), 1222–1227.

Wyman, C.E., 2007. What is (and is not) vital to advancing cellulosic ethanol. Trends Biotechnol. 25 (4), 153–157.